学校编码：10384　　分类号_____密级_____
学号：19820060153187　　UDC_____

厦门大学

博 士 学 位 论 文

异核分子间多量子相干性质与不均匀场下高分辨 NMR 方法研究

Heteronuclear Intermolecular Multiple Quantum Coherences and High-Resolution NMR in Inhomogeneous Magnetic Fields

张 文

指导教师名称：蔡淑惠　教授

专 业 名 称：无线电物理

论文提交日期：2010 年 04 月

论文答辩时间：2010 年 05 月

学位授予日期：2010 年 09 月

答辩委员会主席：_____

评　　阅　　人：_____

2010 年 05 月

厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下独立完成的研究成果。本人在论文写作中参考的其他个人或集体的研究成果均在文中以明确方式标明，并符合法律规范和《厦门大学研究生学术活动规范（试行）》。

另外，该学位论文为（　　）课题（组）的研究成果，获得（　　）课题（组）经费或实验室的资助，在（　　）实验室完成。（请在以上括号内填写课题或课题组负责人或实验室名称，未有此项声明内容的，可以不作特别声明。）

声明人（签名）：

年　　月　　日

厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

（　　）1、经厦门大学保密委员会审查核定的保密学位论文，于　　年　　月　　日解密，解密后适用上述授权。

（　√　）2、不保密，适用上述授权。

（请在以上相应括号内打“√”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。）

声明人（签名）：

年　　月　　日

专用缩写词英汉对照表

1D = One-Dimensional	一维
2D = Two-Dimensional	二维
COSY = COrrelated SpectroscopY	相关波谱
CPMG = Carr–Purcell–Meiboom–Gill	CPMG 序列
CRAZED = COSY Revamped by Asymmetric Z-gradient Echo Detection	不对称 z 向梯度回波检测改进的 COSY
CSG = Coherence Selection Gradient	相干选择梯度
CTP = Coherence Transfer Pathway	相干转移路径
DDF = Distant Dipole Field = Dipolar Demagnetizing Field	远程偶极场 偶极退磁场
DMSO = DiMethyl SulphOxide	二甲基亚砜
DQC = Double-Quantum Coherence	双量子相干
DQF = Double-Quantum Filtered	双量子滤波
fMRI = functional Magnetic Resonance Imaging	功能磁共振成像
FT = Fourier Transform	傅立叶变换
FID = Free Induction Decay	自由感应衰减信号
HOMOGENIZED = HOMOGeneity ENhancement by Intermolecular ZEro-quantum Detection	分子间零量子检测的均匀性增强
IDEAL = Intermolecular Dipolar-interaction Enhanced All Lines	分子间偶极相互作用增强谱线分辨率
iDQC = intermolecular Double-Quantum Coherence	分子间双量子相干
iDQF = intermolecular Double-Quantum Filter	分子间双量子滤波
iMQC = intermolecular Multiple-Quantum Coherence	分子间多量子相干
iSQC = intermolecular Single-Quantum Coherence	分子间单量子相干
iZQC = intermolecular Zero-Quantum Coherence	分子间零量子相干
MAS = Magic Angle Spinning	魔角旋转
MEK = Methyl Ethyl Ketone	甲乙酮
MQC = Multiple-Quantum Coherence	多量子相干
MQF = Multiple-Quantum Filtered	多量子滤波

MRI = Magnetic Resonance Imaging	磁共振成像
MRS = Magnetic Resonance Spectroscopy	磁共振波谱
MSE = Multiple Spin Echoes	多自旋回波
NMR = Nuclear Magnetic Resonance	核磁共振
NOE = Nuclear Overhauser Effect	核 Overhauser 效应
NOESY = Nuclear Overhauser Effect SpectroscopY	NOE 谱
PFG = Pulsed Field Gradient	脉冲梯度场
RF = Radio Frequency	射频
SECSY = Spin Echo Correlated SpectroscopY	自旋回波相关波谱
SEL-HOMOGENIZED	选择性 HOMOGENIZED
SQC = Single-Quantum Coherence	单量子相干
TSCTES = Total Spin Coherence Transfer Echo Spectroscopy	全自旋相干转移回波波谱
WATERGATE = WATER suppression by GrAdient-Tailored Excitation	梯度裁剪激励的水峰压制，水门
ZQC = Zero-Quantum Coherence	零量子相干

目　录

CONTENTS

作者姓名：张 文

论文题目：异核分子间多量子相干性质与不均匀场下高分辨NMR方法研究

作者简介：张 文，女，1981年12月出生，2004年09月师从于厦门大学蔡淑惠教授，于2010年09月获博士学位。

中 文 摘 要

自1990年发现iMQC现象以来，关于iMQC性质及其应用的研究便成为NMR领域的一个热门课题。iMQC来源于核自旋间的远程偶极相互作用，因此iMQC信号具有不同于常规单量子信号的一些特性。目前iMQC已在许多方面特别是不均匀场下高分辨NMR中得到应用。另一方面，随着NMR应用范围的不断扩大，有关四极核的NMR研究越来越受到重视。基于四极核iMQC的NMR和MRI对分析化学和生物医学等领域的研究具有重要的意义。本论文着重对包含四极核的自旋体系的iMQC信号的性质进行分析和表征，主要工作有：

一、系统分析了多种不均匀场下高分辨NMR方法，特别是基于iMQC、章动回波和空间编码技术的高分辨方法的性质及其机理，比较和总结了这些方法的优缺点，为后续的高分辨NMR研究打下了坚实的基础。

二、利用IDEAL-II脉冲序列对iDQC高分辨方法在中等至较大不均匀磁场中的适用性进行研究，考察了选择性脉冲设置、磁场不均匀性大小和样品差异三个因素对iDQC谱图质量的影响。实验与模拟结果表明，当磁场不均匀度达到一定程度时，由于溶剂自旋与溶质自旋共振频率发生重叠，选择性脉冲无法仅仅选择激发溶剂，导致谱图受到杂信号的干扰，甚至完全无法得到化学位移的信息。此外，由于脉冲的选择激发效果与溶剂和溶质间的最小共振频率差有关，不同的样品在相同的不均匀场下得到的谱图质量也可能不同。

三、应用异核CRAZED序列观测自旋1/2和自旋3/2核间的iMQC信号，研究信号强度与射频脉冲翻转角之间的关系。以单自旋双组分体系为模型，采

用升降算符理论推导出iMQC信号的解析表达式。理论和实验结果表明，自旋1/2核与自旋3/2核的iMQC信号强度对射频脉冲翻转角有相同的依赖关系。在此基础上进一步比较*IS* (*I*=1/2, *S*=3/2)体系和*IS* (*I*=1/2, *S*=1/2,1; *I*=1, *S*=1/2)体系的iMQC信号强度与射频脉冲翻转角之间的关系，可以看到在液体状态下，异核iMQC信号强度与射频脉冲翻转角的关系遵循相同的规律。

四、以氘代样品为例，首次观测到自旋1核间的iMQC信号。从理论上和实验上研究了自旋1体系在CRAZED序列作用下产生的iMQC信号强度与射频脉冲翻转角的关系。研究结果表明，液体状态下自旋1体系内同核iMQC信号强度与脉冲翻转角之间的关系与自旋1/2体系是一样的。这一结论适用于所有自旋1体系，无论核电四极矩大或者小。

五、提出了基于异核iSQC和iDQC的两个改进型CRAZED序列以快速获得不均匀磁场下高分辨NMR谱。利用升降算符理论推导得到由两个脉冲序列获得的信号的解析表达式。实验结果验证了这两个脉冲序列的有效性。由于F1维谱宽只与磁场不均匀性有关，与溶质的化学位移无关，实验时间可大大缩短。值得一提的是，基于异核iSQC的改进型CRAZED序列是异核iSQC在高分辨NMR研究中的首次应用。

关键词：核磁共振；分子间多量子相干；不均匀磁场；高分辨谱；四极核

Heteronuclear Intermolecular Multiple Quantum Coherences and High-Resolution NMR in Inhomogeneous Magnetic Fields

Wen Zhang

ABSTRACT

Research on the properties and applications of intermolecular multiple quantum coherences (iMQCs) has become a hot topic in the NMR community since the discovery of iMQC phenomena in 1990s. The iMQC signals are originated from intermolecular dipole-dipole interaction and have some unique properties different from conventional SQCs. IMQCs have found many applications in many areas, especially in high-resolution NMR spectroscopy in inhomogeneous fields. On the other hand, with the extension of NMR application field, there has been increasing interest in high natural abundant quadrupolar nuclei. The iMQCs involving quadrupolar nuclei may be of great value for analytical chemistry, biology and medicine, etc. The work of this thesis focuses on the analysis and characterization of iMQC signals in the systems containing quadrupolar nuclei. The main works are summarized as follows:

1. The main existing high-resolution methods were analyzed systematically, especially the properties and mechanisms of the methods based on iMQCs, nutation echoes and spatial encoding respectively. Comparisons between these methods were made, and their advantages and shortages were revealed. This part of work provides the bases for the following researches on high-resolution NMR spectroscopy.

2. Taking the IDEAL-II pulse sequence as an example, the applicability of high-resolution iDQC methods in moderate to severe inhomogeneous magnetic fields was studied. The effects of RF pulse selectivity, magnetic field inhomogeneity and sample difference on spectral quality were analyzed.

Experimental and simulation results show that once the field inhomogeneity reaches a certain degree, the overlap of solvent and solute peaks will make the RF pulses impossible to selectively excite desired peaks, which results in the appearance of undesirable peaks. In addition, the spectral quality may vary with sample even in the same inhomogeneous fields, depending on the chemical shift distributions and the *J* coupling networks of the system under study.

3. The heteronuclear iMQC signals from *IS* (*I*=1/2, *S*=3/2) spin system was detected by using heteronuclear CRAZED pulse sequence. The dependences of signal intensity on RF pulse flip angles were investigated. Analytical signal expressions were deduced based on the raising and lowering operators. Theoretical and experimental results show that the dependences of spin-1/2 iMQC signal intensities on the RF pulse flip angles follow the same rules as that of spin-3/2 iMQC signal. The results are in accordance with heteronuclear iMQCs of *IS* (*I*=1/2, *S*=1/2 or 1; *I*=1, *S*=1/2) spin systems, implying that heteronuclear iMQCs have the same properties in liquid state NMR.

4. The iMQC signals between spin-1 nuclei were observed for the first time using a deuterated sample as an example. The signal intensity as a function of RF pulse flip angles in the CRAZED experiments was studied theoretically and experimentally. The results demonstrate that the relationships between iMQC signal intensity and RF pulse angles for spin-1 and spin-1/2 nuclei are the same. The relations are applicable to all kinds of spin-1 nuclei in homogeneous liquid state, no matter the electric quadrupolar moment is small or large.

5. Two new pulse sequences based on heteronuclear iSQCs and iDQCs were proposed to achieve fast acquisition of high-resolution spectra in inhomogeneous fields. Analytical expressions for the signals from the two sequences were deduced based on the raising and lowering operators. Experiments were performed to validate the feasibility of the two sequences. Because the width of the F1 dimension is determined by the line-broadening instead of chemical-shift of the detected spins, the total acquisition time is greatly reduced. It is the first time to obtain high-resolution spectra in inhomogeneous fields via heteronulcear iSQCs.

Keywords: NMR; intermolecular multiple-quantum coherence; inhomogeneous magnetic field; high-resolution spectra; quadrupolar nuclei